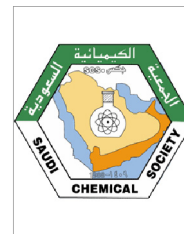




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ORIGINAL ARTICLE

Synthesis and surface-active property of diethanolamide and epoxidised diethanolamide surfactant from the seed oil of *Baphia nitida*



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Abstract Oil was extracted from the seed of *Baphia nitida*, characterised and used in the production of diethanolamide and epoxidised diethanolamide via transamidation reaction. The oil of *B. nitida* had C18:2 ($50.00 \pm 0.20\%$) fatty acid as the most abundant fatty acid. The epoxidised diethanolamide was synthesised by peroxyformic acid generated *in situ* by reacting formic acid and hydrogen peroxide with the oil of *B. nitida*. The formation of the diethanolamide and epoxidised diethanolamide was monitored and confirmed using FTIR and ^1H NMR. The epoxidised diethanolamide showed better surface-active properties than the diethanolamide in terms of emulsion stability, and foaming power.

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1. Introduction

The most important property of the fatty acids and their derivatives for oleochemical purposes is their amphiphilic nature. This means that a part of the molecule (the alkyl chain) is lipophilic (hydrophobic) while the other part (the head group) is hydrophilic (lipophobic). As a result, the molecule can exist comfortably at an oil water interface and can reduce the surface tension at such interfaces. This property is fundamental

in all living systems and also in many food and other man-made systems where aqueous and fatty phases must co-exist. It confers surface activity (hence such compounds are called surfactants) which allows appropriate compounds to act as emulsifying agents, detergents, lubricants, etc. The simplest and oldest examples are soaps such as sodium palmitate and oleate. The alkyl chain is lipophilic and the carboxylate group is hydrophilic. The detergent properties of such compounds have been exploited for a long time.

The use of surfactant in various areas is based on its special physicochemical properties, particularly its ability to form several supra-molecular structures, such as micelles, liquid crystals, liposomes or vesicles, monolayers, bilayers, and multilayers, through adsorption and aggregation (Zhao and Zhu, 2003). The application of surfactants cuts across both edible and non edible applications. The monostearate and oleate glycerides are used mainly in the food industry where they act as viscosity modifiers and stabilisers that provide texture to

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processed foods (Van Haften, 1979). Non edible industrial applications of surfactants are numerous and they are important components in formulations of agrochemicals, corrosion inhibitors, cosmetics, detergents, lubricants, metal works and oil drilling fluids, polymers, and textile finishes (Lynn and Bory, 1997). They are surface active agents that reduce surface tension of liquid; they may act as detergents, wetting agents, emulsifiers, foaming agents and dispersants.

A number of synthetic or petroleum based surfactants are known to be toxic to animals, ecosystem and humans and can increase the diffusion of other environmental contaminants (Emmanuel et al., 2005; Metcalfe et al., 2008). Despite being toxic, some of these surfactants are routinely deposited in numerous ways on land and in water systems. Though, some such as the linear alkyl benzene sulphonates (LAS) and alkyl phenol ethoxylates (APE) have been reported to break down in aerobic conditions found in sewage treatment plants and in soil (Scott and Jones, 2000). So there is still a need to produce low cost surfactants that are ecofriendly, and biodegradable from sources that are renewable and readily available.

Seed oils are sources of fatty acids which are renewable and cheap that can be used in the production of surfactant. *Baphia nitida* is an underutilised plant in Nigeria which is about 10 m high with trunk to about 45 cm in diameter and slender branches forming an umbrella-shaped crown; usually an under storey tree of wetter parts of the coastal area. The tree is often planted in the villages as an ornamental or shade and as a source of medicines and dye (Burkill, 1995). Previous study showed the proximate composition of the seed, metal composition of the seed and oil and the physicochemical properties of the oil with an oil yield of $27.14 \pm 0.20\%$ from the seed (Adewuyi et al., 2009).

In this study, diethanolamide and epoxidised diethanolamide were prepared from the seed oil of *B. nitida* and their properties compared. Diethanolamide was produced from the oil by reacting it with diethanolamine in the presence of sodium methoxide catalyst. A chemical modification was carried out on the oil to produce the epoxidised diethanolamide. The oil was epoxidised via performic acid generation *in situ* in a one-pot multi-step reaction system and later reacted with diethanolamine in the presence of sodium methoxide catalyst to form the epoxidised diethanolamide. The epoxidation of the oil of *B. nitida* and formation of diethanolamide as well as epoxidised diethanolamide were monitored using Fourier Transform Infrared Spectroscopy (FTIR) and Nuclear Magnetic Resonance (^1H NMR).

2. Materials and methods

2.1. Materials

The mature seeds of *B. nitida* were collected from the trees grown at the garden of the University of Ibadan, Ibadan, Oyo state, Nigeria. They were identified at the herbarium unit, Botany Department University of Ibadan. Formic acid (100%) and hydrogen peroxide (30%) were purchased from Merck, Darmstadt, Germany. All solvents and chemicals used in this study were of analytical grade and were purchased from S.D. Fine Chemicals, Mumbai.

2.2. Chemical analysis of the oil of *B. nitida*

The dried seeds of *B. nitida* were extracted with *n*-hexane for 10 h. using soxhlet extractor (Oderinde et al., 2008). The extracted oil was analysed for its iodine, saponification and free fatty acid content by a method described by the Association of Official Analytical Chemist (AOAC, 1994).

2.3. Fatty acid composition of the oil of *B. nitida*

Fatty acid methyl esters of both the oil were prepared by refluxing the oil at 70 °C for 4 h. in 2% sulphuric acid in methanol. The esters were extracted into ethyl acetate, washed free of acid and passed over anhydrous sodium sulphate. The ethyl acetate extracts were further concentrated using a rotary evaporator. The fatty acid composition was analysed using an Agilent 6890N series gas chromatography equipped with FID detector on a split injector. A fused silica capillary column (DB-225, 30 m \times 0.32 mm i.d., J&W Scientifics, USA) was used with the injector and detector temperature maintained at 230 and 250 °C, respectively. The oven temperature was programmed at 160 °C for 2 min and finally increased to 230 °C at 4 °C/min. The carrier gas was nitrogen at a flow rate of 1.5 mL/min. The area percentages were recorded with a standard Chemstation Data System.

2.4. Epoxidation of the oil of *B. nitida*

The epoxidation was carried out in a 150-mL three-necked round-bottom flask equipped with a thermometer sensor and a mechanical stirrer. The whole apparatus was kept in a water bath to maintain the desired temperatures. 45.20 g (0.0482 mol) of the oil and 4.9 g (0.106 mol) of 100% formic acid were placed in the flask and cooled to a temperature of 15 °C while stirring. 46.1 g (0.407 mol) of hydrogen peroxide was added dropwise with continuous stirring for about 30 min. This precaution was taken to prevent overheating of the system due to the exothermic nature of epoxidation reactions. The temperature was later raised to 70 °C and maintained at this temperature for 3 h with aliquots been taken at every 30 min interval and analysed using FTIR. After the formation of epoxide, the mixture was cooled to room temperature and the epoxidised oil was extracted with ethyl acetate, washed with water until free of acid and passed over sodium sulphate. This was later concentrated using a rotary evaporator. The reaction scheme is presented in Fig. 1. The percentage Oxirane value of the epoxidised oil was determined by the AOCS method (1997).

2.5. Synthesis of diethanolamide from the oil of *B. nitida*

The reaction was carried out in a round bottom Pyrex glass reaction flask submerged in an oil bath. The reaction flask was equipped with a mechanical stirrer, thermometer and condenser. Diethanolamine was reacted with the oil at a molar ratio of 6:1 (diethanolamine:oil) in the presence of sodium methoxide (2% by weight of diethanolamine and oil). The reaction was carried out at a temperature of 115 °C while the formation of the diethanolamide was monitored with TLC. At the end of the reaction, the reaction mixture was allowed

A Formation of peroxyacid (Okieimen et al., 2002; Rangarajan et al., 1995)



B Epoxidation (Okieimen et al., 2002; Rangarajan et al., 1995)



Figure 1 Reaction scheme for the synthesis of epoxidised oil. (See above-mentioned references for further information.)

to cool and was later dissolved in diethyl ether in a separating funnel. The ether phase was washed with 5% aqueous hydrochloric acid. The ether layer was separated, washed with water and passed over sodium sulphate. The resulting ether layer was later concentrated using a rotary evaporator. The scheme for this reaction is shown in Fig. 2.

2.6. Synthesis of epoxidised diethanolamide from the oil of *B. nitida*

The reaction was also carried out in a round bottom Pyrex glass reaction flask submerged in an oil bath. The reaction flask was equipped with a mechanical stirrer, thermometer and condenser. Diethanolamine was reacted with the epoxidised oil at a molar ratio of 6:1 (diethanolamine:oil) in the presence of sodium methoxide (2% by weight of diethanolamine and oil). The reaction was carried out as described above for the unepoxidised oil as shown in Fig. 3.

2.7. Evaluation of surface-active properties of diethanolamide and epoxidised diethanolamide

2.7.1. Emulsion stability

Emulsifying power of the aqueous solutions of surfactants was determined for water/liquid paraffin system. Aqueous solution

(0.5%) of the diethanolamide, epoxidised diethanolamide and reference surfactants (sodium lauryl sulphate) were prepared. 20 ml of aqueous solution of diethanolamide and epoxidised diethanolamide was separately taken in a 100 ml stoppered graduated measuring cylinder and 20 ml of paraffin was poured into the measuring cylinder through the side of its wall. The cylinder containing solution was turned upside down a total of 30 times at a rate of 1 turn per 2 s. The time of separation of the aqueous phase for 15 ml was noted. The method was simple and worked well (Ware et al., 2007).

2.7.2. Wetting power

Wetting power of the aqueous solutions of surfactants in distilled water was determined using the Canvas Disc Method (McCutecheon, 1950).

2.7.3. Foaming power

Aqueous solution (0.5%) of the surfactants and reference surfactant were prepared. 20 ml aqueous solution was poured into a 100 ml graduated cylinder. The cylinder containing the solution was turned upside down a total of 30 times at a rate of 1 turn per 2 s. The foam produced (in mm) was measured immediately and after 5-min interval. These data were used for estimating the foamability and foam stability of the surfactant (Hughes and Lew, 1970).

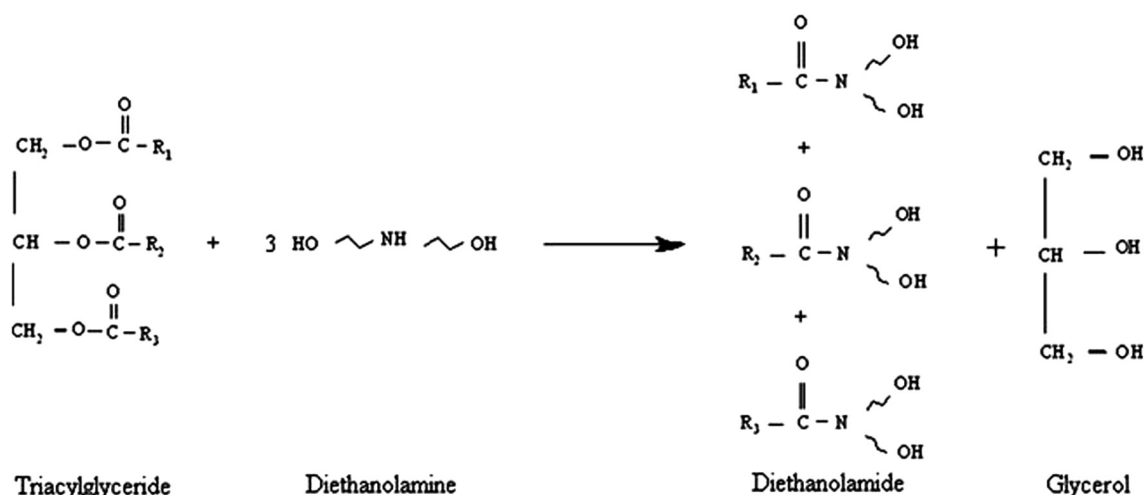


Figure 2 Reaction scheme for the synthesis of diethanolamide. R_1 , R_2 and R_3 are alkyl chains without epoxide(s) functional group.

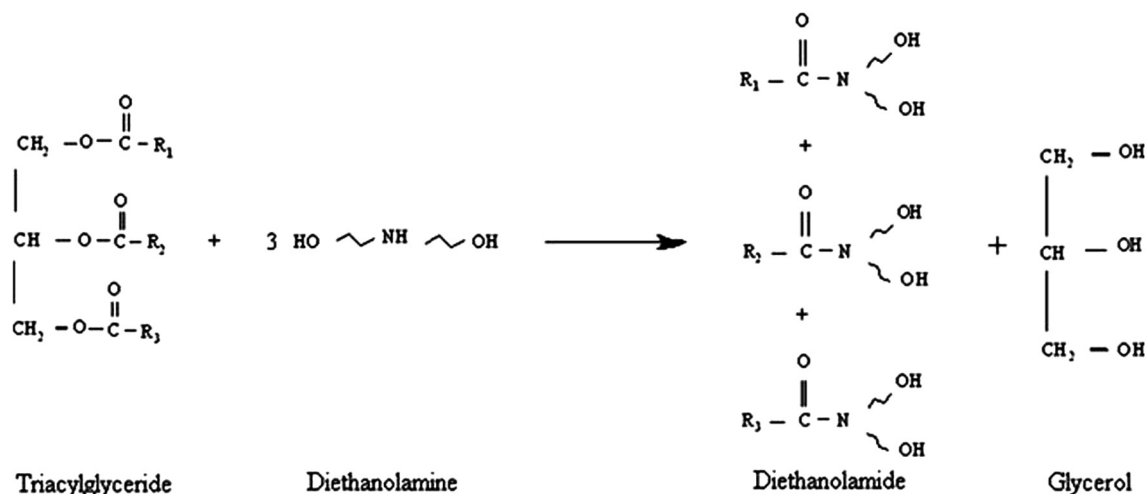


Figure 3 Reaction scheme for the synthesis of epoxidised diethanolamide. R_1 , R_2 and R_3 are alkyl chains with epoxide(s) functional group.

2.7.4. Surface tension

KRUSS Processor Tensiometer K 100 was used. The surface tension of 0.5% aqueous solution of surfactants was determined as given in the technical literature and ASTM designation D 1331-56 (2001).

2.8. Fourier transform infrared (FTIR)

The FTIR spectra of oil, epoxidised oil and amides were recorded using a Perkin Elmer FTIR system spectrum BX LR64912C. The samples were spread over NaCl discs, and their spectra were recorded in the range of $4000\text{--}400\text{ cm}^{-1}$.

2.9. Nuclear magnetic resonance (NMR) spectroscopy

^1H NMR spectra of oil, epoxidised oil and amides were obtained using a 300 MHz Bruker NMR spectrophotometer in CDCl_3 containing some amount of TMS as internal standard.

3. Results and discussion

3.1. Physicochemical properties and fatty acid composition of *B. nitida*

Table 1 presents the result of the physicochemical properties of *B. nitida*. The saponification value of *B. nitida* was found to be $184.80 \pm 0.60\text{ mgKOH/g}$ while the free fatty acid was $1.23 \pm 0.01\%$. C18:2 (50.00 \pm 0.20%) fatty acid was the most abundant fatty acid found in *B. nitida* as shown in Table 2. The

Table 2 Fatty acid composition (%) of *B. nitida* seed oil.

Fatty acids	<i>Baphia nitida</i>
16:0	1.60 \pm 0.50
18:0	1.80 \pm 0.10
18:1	15.90 \pm 0.50
18:2	50.00 \pm 0.20
18:3	0.70 \pm 0.10
20:0	0.80 \pm 0.10
20:1	2.80 \pm 0.30
22:0	17.00 \pm 0.10
22:1	1.30 \pm 0.50
24:0	8.1 \pm 0.30
Unsaturated	70.70 \pm 0.20
Saturated	29.30 \pm 0.30

Values are mean \pm standard deviation of triplicate determinations.

fatty acid results have been previously documented by Adewuyi and Oderinde (2013). C18:1 was found as 15.90 \pm 0.50% while C22:0, a long chain fatty acid was found as 17.00 \pm 0.10%. The oil *B. nitida* had an unsaturation of 70.70 \pm 0.20%. This unsaturation is indicative of the possibility of modifying the oil since the unsaturated point is a site at which other functional groups could be introduced into the oil.

3.2. Epoxidation of the oil

Epoxidation of the oil of *B. nitida* was achieved via performic acid generation *in situ* in a one-pot multi-step reaction system. *In situ* epoxidation was carried out using formic acid and hydrogen peroxide. This reaction was characterised by two main reaction steps which included the formation of peroxoformic acid (peroxoformic acid) and formation of epoxides as represented in Fig. 1. The first step is the acid-catalysed formation of peroxoformic acid from formic acid while the second step is the uncatalysed epoxidation of the oil with the peroxoformic acid which was monitored using FTIR. Aliquots were taken at an interval of 30 min to check the progress of the reaction. The percentage oxirane oxygen content of the epoxidised oil of *B. nitida* was found to be 4.20 \pm 0.20%.

Table 1 Physicochemical properties of the *Baphia nitida*.

Parameter	<i>Baphia nitida</i>
Free fatty acid (%)	1.23 \pm 0.01
Iodine value (g iodine/100 g)	138.38 \pm 0.50
Saponification value (mgKOH/g)	184.80 \pm 0.60

Values are mean \pm standard deviation of triplicate determinations.

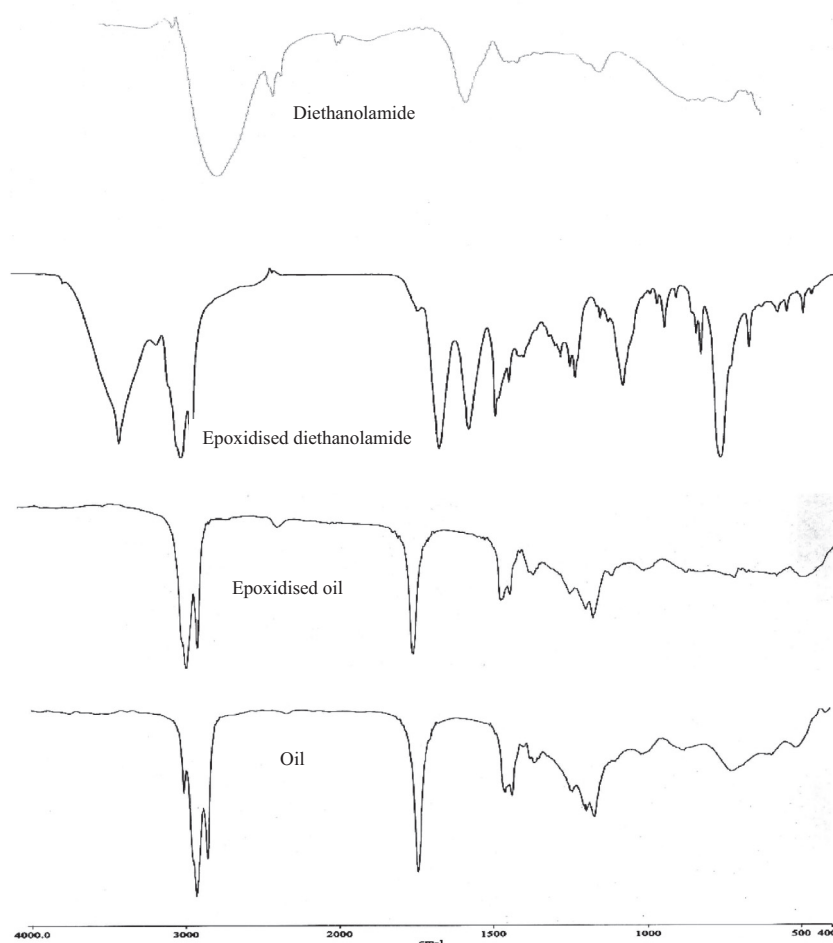


Figure 4 FTIR spectra of the oil, epoxidised oil, epoxidised diethanolamide and diethanolamide.

Fig. 4 shows the FTIR result of the oil, epoxidised oil, epoxidised diethanolamide and diethanolamide. The characteristic peak at 3003.10 cm^{-1} was attributed to the C—H stretching of $\text{C}=\text{C}-\text{H}$ in the oil of *B. nitida* indicating the presence of unsaturated functional groups in the oil which was not detected in the spectra of the epoxidised oil indicating that epoxidation has taken place in the oil. The presence of peak at 834 cm^{-1} in the epoxidised oil confirms the formation of epoxides. This peak is due to the symmetric in-plane deformation of the epoxy group. Also, the peak at 1250 cm^{-1} may be attributed to the symmetric ring stretching of the epoxy group. The proton NMR spectra of the oil, epoxidised oil, epoxidised diethanolamide and diethanolamide are shown in Fig. 5. The ethylene protons were observed at 5.5 ppm in the oil. This signal was only found in the oil indicating the presence of unsaturation only in the oil and not in the epoxidised oil and epoxidised diethanolamide. The disappearance of this signal in the epoxidised oil showed that epoxidation has taken place. The epoxy protons were observed at 2.9 ppm in the epoxidised oil.

3.3. Synthesis of diethanolamide and epoxidised diethanolamide

In Fig. 4, the peak at 2927 cm^{-1} was accounted for as being the C—H stretching of $-\text{CH}_3$. The C=O vibrational frequency of

ester at 1743 cm^{-1} was only found in the oil and epoxidised oil. This C=O stretching frequency of ester functional groups at 1743 cm^{-1} was not found in the amide indicating the conversion of the esters to amide. The values 1458 cm^{-1} and 1169 cm^{-1} , which are common to the spectra of the oil and epoxidised oil, may be attributed to the C—H bending frequency of saturated alkane and C—O stretching frequency of ester respectively. The band at 3317 cm^{-1} was found in the alkanolamide which may be attributed to the frequency of vibration of the OH group. The peak at 1645 cm^{-1} was also found only in amide. This peak was formed as the C=O frequency (1743 cm^{-1}) of esters disappeared and it can be accounted for as being the C=O frequency of tertiary amide.

The ^1H NMR spectra of the diethanolamide and epoxidised diethanolamide as well as the oil and epoxidised oil are presented in Fig. 5. The methyl groups of the esters were seen at 2.6–2.8 ppm. The peaks of the terminal methyl groups were found at 0.5–1.0 ppm while the signal at 2.9 ppm in the epoxidised diethanolamide could be assigned to the contribution from the hydroxyl groups which may have resulted from the opening of some of the epoxy rings during reaction. The signal at 5.5 ppm in the oil may be accounted for as being those of ethylene proton. This signal was not found in the epoxidised oil indicating the conversion of the unsaturated bonds ($-\text{C}=\text{C}-$) to epoxides. Signals at 4.5 and 4.7 ppm in both

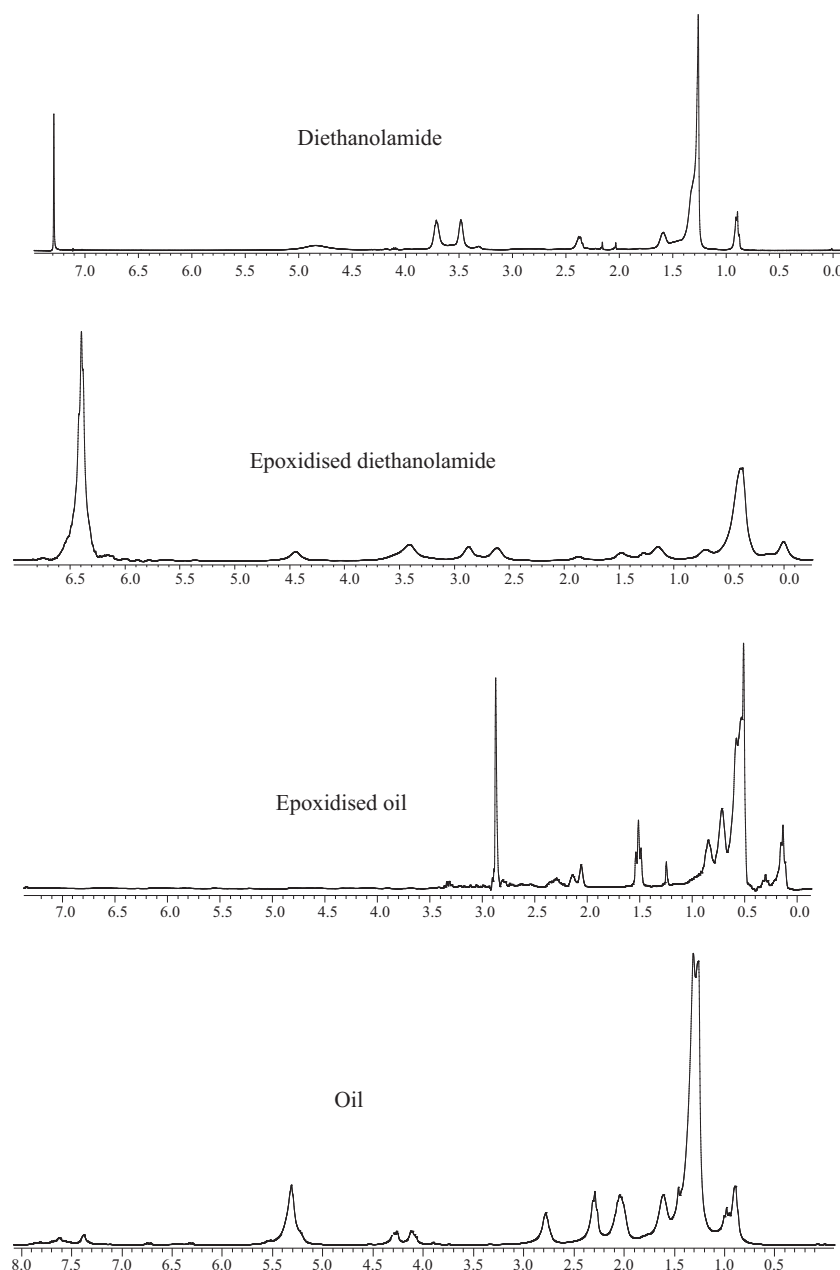


Figure 5 ^1H NMR of the oil, epoxidised oil, epoxidised diethanolamide and diethanolamide.

the epoxidised diethanolamide and diethanolamide were assigned to the terminal hydroxyl groups of these amides. The signals found at 3.6 ppm in the epoxidised diethanolamide may be due to the contribution from the methine group of the oxirane. The signals at 6.8 ppm in the epoxidised diethanolamide and 6.6 ppm in the diethanolamide represent the protons of the amide formed.

3.4. Evaluation of surface-active properties of diethanolamide and epoxidised diethanolamide

The surface-active properties of the synthesised diethanolamide, epoxidised diethanolamide and known reference anionic surfactant (sodium lauryl sulphate) were determined and

Table 3 Surface-active properties of diethanolamide and epoxidised diethanolamide from *Baphia nitida*.

Surfactant	Emulsion stability (s)	Wetting property (s)	Foaming power (min)
DEA	110.00 \pm 0.10	28.00 \pm 0.30	2.00 \pm 0.30
EDEA	160.00 \pm 0.30	72.00 \pm 0.10	5.00 \pm 0.10
SLS	29.00 \pm 0.50	4.00 \pm 0.50	150.00 \pm 0.10

DEA = Diethanolamide, EDEA = Epoxidised diethanolamide, SLS = Sodium lauryl sulphate.

presented in Table 3. The emulsifying power was judged by the time required for a separation of 15 ml aqueous layer for

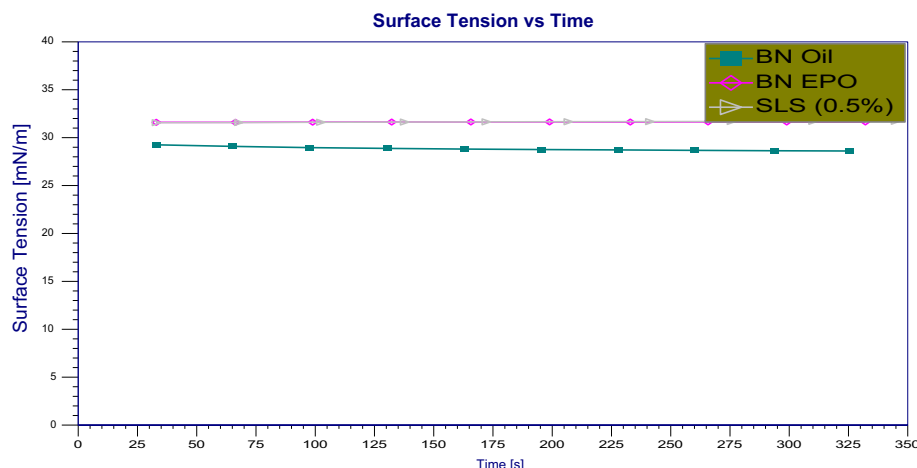


Figure 6 Surface tension of the diethanolamide (BN), epoxidised diethanolamide (BN EPO) and sodium lauryl sulphate (SLS).

the emulsions made under similar condition. The epoxidised diethanolamide (160.00 ± 0.30 s) of *B. nitida* had better emulsion stability than the diethanolamide and the reference surfactant. The reference standard (4.00 ± 0.50 s) showed a better wetting property than those of the diethanolamide and epoxidised diethanolamide. Though, the wetting ability of the diethanolamide (28.00 ± 0.30 s) was better than that of the epoxidised diethanolamide (72.00 ± 0.10 s) indicating that diethanolamide was a better detergent than epoxidised diethanolamide since compounds with short wetting time have good detergency (Ware et al., 2007).

The foaming behaviour of diethanolamide and epoxidised diethanolamide was compared with that of sodium lauryl sulphate. The foaming power of sodium lauryl sulphate was found better than those of the synthesised surfactants. Surfactants are surface agents which have the capacity of reducing the surface tension of liquid. The surface tension is presented in Fig. 6. The surface tension of diethanolamide was 28.69 mN/m, epoxidised diethanolamide was 31.64 mN/m and sodium lauryl sulphate was 31.69 mN/m.

4. Conclusions

The seed oil of *B. nitida* was used in the synthesis of diethanolamide and epoxidised diethanol amide via transamidation reaction. The property of the diethanolamide surfactant was modified by introducing the epoxy functional group into the unsaturated sites of the oil of *B. nitida* using epoxidation reaction. The GC result revealed C18:2 ($50.00 \pm 0.20\%$) as the dominant fatty acids in the oil of *B. nitida*. The epoxidised diethanolamide showed better surface-active properties than the diethanolamide in terms of emulsion stability and foaming power.

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